

(19)



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Office européen des brevets



(11)

EP 0 810 278 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
03.12.1997 Bulletin 1997/49

(51) Int. Cl.⁶: **C10G 25/00**

(21) Application number: **97102446.8**

(22) Date of filing: **14.02.1997**

(84) Designated Contracting States:
DE NL

(30) Priority: **30.05.1996 JP 158862/96**

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(54) Process for eliminating mercury from liquid hydrocarbons

(57) A process for continuously eliminating mercury and mercury compounds in liquid hydrocarbons for example, a natural gas condensate comprising: (a) bringing liquid hydrocarbons containing mercury and mercury compounds, as well as asphaltene into contact, in a first adsorption treatment zone, with a porous inorganic adsorbent which is at least one of materials selected from the group consisting of activated carbon, activated clay, alumina, silica gel, silica-alumina and zeolite, and then (b) bringing the liquid hydrocarbons from the adsorption treatment zone after the adsorption treatment into contact, in a second adsorption treatment zone, with an activated carbon having a specific surface area from 200 m²/g to 2500 m²/g and an average pore diameter from 10 Å to 100 Å. Mercury and mercury compounds in liquid hydrocarbons containing a great amount of heavy ingredients such as asphaltene can be eliminated continuously for a long period of time.

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Description

The present invention concerns a process for eliminating mercury and mercury compounds from liquid hydrocarbons containing a great amount of sulfur compounds and asphaltene such as natural gas condensates, particularly, heavy condensates recovered from natural gases. The present invention relates more specifically to a process for substantially complete elimination of mercury and mercury compounds coexisting with asphaltene and the like in natural gas condensates continuously for a long period of time.

Most of natural gas condensates contain elemental mercury and mercury compounds such as organic and inorganic mercury, and the content sometimes reaches as high as from several tens ppb to several thousands ppb while depending on the place of origin. If natural gas condensates or naphthas obtained by distillation of them containing such mercury and mercury compounds, are used as a feedstock for olefins for petrochemical products, for example, ethylene or propylene, or when they are used as a feedstock for a reformer for hydrogen production, aluminum material used for the constituent material of the apparatus may bring about amalgam corrosion or poisoning is caused to noble metal catalysts used for hydrogenation in the case where they are used as feedstocks for petrochemical product.

Accordingly, various process for eliminating mercury contained in liquid hydrocarbons have been studied and various kinds of mercury adsorbents and processes for eliminating mercury by using them have been proposed. For example, sulfides of heavy metals such as molybdenum, tungsten and vanadium carried on supports such as alumina have been proposed as the mercury adsorbent (refer, for example, to Japanese Patent Publication No.24623/1994) and, further, mercury adsorbents comprising sulfur carried on porous supports, for example, a sulfur-carrying activated carbon obtained by mixing activated carbon with fine sulfur particles and heating them to a predetermined temperature (refer to Japanese Patent Laid-Open No. (7891/1984) or activated carbon containing organic sulfur compounds (refer to Japanese Patent Laid-Open No.114632/1987) have been disclosed.

Further, as the process for eliminating mercury in natural gas condensates, there has been proposed, for example, a process of bringing mercury compound-containing natural gas condensates into contact with a γ -alumina catalyst, a zeolite catalyst and/or a silica catalyst at a temperature from 150°C to 300°C thereby decomposing the mercury compounds into elemental mercury and then eliminate the resultant elemental mercury with an adsorbent mainly comprising molybdenum sulfide (refer to Japanese Patent Laid-Open No.33091/1994). However, decomposition of the mercury compounds into elemental mercury by the γ -alumina catalyst, zeolite catalyst or silica catalyst requires high temperature and the catalyst is poisoned by asphaltene or the like in the adsorptive elimination of mercury under the coexistence of heavy ingredients such as asphaltene, making it difficult to maintain the mercury adsorbability for a long period of time, and no suitable process applicable to a long time continuous operation has yet been developed.

An object of the present invention is to provide a process for eliminating mercury and mercury compounds existing in liquid hydrocarbons containing heavy ingredients such as asphaltene and resinous materials with no effect of asphaltene and the like and efficiently for a long period of time irrespective of the form of them existing therein.

Another object of the present invention is to provide a process for adsorption-elimination of mercury and mercury compounds existing in liquid hydrocarbons containing asphaltene and resinous materials in a simple device, by convenient operation and efficiently for a long period of time.

A further object of the present invention is to provide a process for eliminating mercury and mercury compounds in natural gas condensates containing mercury substantially completely by using an adsorbent.

A still further object of the present invention is to provide an adsorbent for adsorption-elimination of mercury and mercury compounds coexisting with asphaltene and resinous materials in liquid hydrocarbons.

Other objects and advantages of the present invention will become apparent by reading the following descriptions of the present specification.

It is to be noted that the term "mercury" used in the present invention includes organic and inorganic compounds unless otherwise specified.

Then, in view of the situations for the development of a process for eliminating mercury and mercury compounds in liquid hydrocarbons of natural gas condensates as described above, the present inventors, et al have made an earnest study for overcoming the foregoing objects and, as a result, have accomplished the present invention based on the finding that continuous elimination of mercury can be practiced efficiently and stably for a long period of time by bringing liquid hydrocarbons containing mercury and asphaltene into contact with a porous inorganic adsorbent and bringing the treated-liquid hydrocarbons into contact with a mercury adsorbent of activated carbon having a predetermined property.

That is, the present invention concerns a process for eliminating mercury and mercury compounds in liquid hydrocarbons, comprising contacting liquid hydrocarbons containing mercury and asphaltene in a first adsorption treatment zone with a porous inorganic adsorbent which is at least one of materials selected from the group consisting of activated carbon, activated clay, alumina, silica gel, silica alumina and zeolite, and then contacting the adsorption-treated liquid hydrocarbons in a second adsorption treatment zone with an activated carbon having a specific surface area from 200 m²/g to 2500 m²/g, an average pore diameter from 10 Å to 100 Å and a pore volume from 0.4 ml/g to 1.5 ml/g.

The unique feature of the present invention is based on the finding obtained by the study of the present inventors, et al, that the mercury adsorbability of an activated carbon having high adsorbability is remarkably lowered in case of

elimination of mercury from liquid hydrocarbons in which heavy ingredients such as asphaltene and resinous materials coexist with mercury, whereas an activated carbon having not so high mercury adsorbability can not completely eliminate mercury but the adsorbability is not so hindered even under the coexistence of asphaltene and the like, and resides in that a mercury elimination process capable of operating continuously for a long period of time can be attained by using a selective combination of two or more different kinds of specific mercury adsorbents.

The present invention further provides, as another preferred embodiment, a process for eliminating mercury in liquid hydrocarbons comprising:

- (a) contacting liquid hydrocarbons containing mercury and mercury compounds and asphaltene in a first adsorption treatment zone with at least one of materials selected from the group consisting of alumina, silica-alumina, zeolite and activated clay having a specific surface area of more than $200 \text{ m}^2/\text{g}$, a pore diameter from 2 \AA to 1000 \AA , and then,
- (b) contacting the liquid hydrocarbons from the first adsorption treatment zone in a second adsorption treatment zone with an activated carbon having a specific surface area from $500 \text{ m}^2/\text{g}$ to $2000 \text{ m}^2/\text{g}$, an average pore diameter from 10 \AA to 50 \AA and a pore volume from 0.4 ml/g to 1.2 ml/g .

Further, the present invention provides, as a preferred embodiment, a process for eliminating mercury in liquid hydrocarbons comprising:

- (a) contacting liquid hydrocarbons containing mercury and asphaltene in a first adsorption treatment zone with an activated carbon having a specific surface area of more than $200 \text{ m}^2/\text{g}$, a pore diameter from 10 \AA to 1000 \AA and an average pore diameter of more than 100 \AA , and
- (b) contacting the adsorption-treated liquid hydrocarbons from the first adsorbing treatment zone in a second adsorption treatment zone with an activated carbon having a specific surface area from $500 \text{ m}^2/\text{g}$ to $1500 \text{ m}^2/\text{g}$, and an average pore diameter from 10 \AA to 30 \AA , and a pore volume from 0.5 ml/g to 1.2 ml/g .

The liquid hydrocarbon used for the process for eliminating mercury and mercury compounds in the liquid hydrocarbons according to the present invention has no particular restriction and there can be mentioned, for example, natural gas condensates recovered from natural gases. For example, some of natural gas condensates from South Asia usually contain 1 % to 3 % by weight of asphaltene. Asphaltene is an asphaltic carbonaceous ingredient which is soluble to benzene but insoluble to pentane and heptane, mainly comprises a number of relatively high molecular weight condensed ring aromatic compounds and contains a great amount of sulfur, oxygen and nitrogen compounds. Further, the natural gas condensates also contain, for example, carbon as an asphalt analogous material and resinous materials as a precursor for asphaltene. Some of natural gas condensates contain more than 1% by weight of asphaltene, etc. but natural gas condensates containing mercury and asphaltene can be treated by the process for eliminating mercury according to the present invention irrespective of the content of the asphaltene and the like. The present inventors, et al have recognized based on a number of experiments that the mercury adsorbability is lowered as the asphaltene content is increased. As a result, it has been found that the mercury adsorbability of the activated carbon in the second adsorption treatment zone can be maintained at a high level by controlling the asphaltene content to less than about 14 ppm. Accordingly, it is possible also in a single adsorption treatment zone to dilute the asphaltene concentration by partially refluxing a treated oil after the adsorption treatment to an untreated oil, thereby improving the mercury elimination rate and increasing the duration of life of the adsorbent.

The process for eliminating mercury in the liquid hydrocarbons according to the present invention is extremely effectively applicable to elimination of mercury in natural gas condensates having compositions as described above, but it can also be used for any of liquid hydrocarbon, naphtha, kerosene, light oil, vacuum distillation oil, pyrolytic gasoline, catalytic naphtha or the like obtained from natural gases or petroleum entraining gases with similar effects.

Mercury in the natural gas condensates is contained in the form of elemental mercury, as well as mercury compounds such as organic or inorganic mercury and the content may sometimes reach from several tens ppb to several thousands ppb while varying according to places of origin but mercury existing in any of the forms can be treated by the process for eliminating mercury in the liquid hydrocarbons according to the present invention without requiring a step of reduction and decomposition of mercury compounds as proposed so far. Further, according to the present invention, mercury in the natural gas condensates can be treated over a wide range of concentration with no restriction of the mercury concentration, and mercury contained even in a great amount can be eliminated substantially completely.

In the process for eliminating mercury in the liquid hydrocarbons according to the present invention, the porous inorganic adsorbent used in the first adsorption treatment zone is selected from the group consisting of activated carbon, activated clay, alumina, silica gel, silica-alumina and zeolite. Porous inorganic adsorbents having specified pore structure are preferred and those having characteristic values with a specific surface area of more than $200 \text{ m}^2/\text{g}$ and a pore diameter from 2 \AA to 1000 \AA can be mentioned.

For the average pore diameter, a relatively large pore diameter is set such that pores of the adsorbent are not

closed by heavy ingredients such as asphaltene. Preferred average pore diameter is from 10 Å to 200 Å. With such por characteristics of the porous inorganic adsorbent, asphaltene and the like can be eliminated preferentially by adsorption.

As the activated carbon used in the first adsorption treatment zone of the present invention, those having a specific surface area of more than 200 m²/g, particularly, from 500 m²/g to 2500 m²/g are more preferred. Further, a preferred range for the pore diameter is from 2 Å to 1000 Å, particularly, from 5 Å to 500 Å and, further preferably from 10 Å to 300 Å. The average pore diameter is from 100 Å to 200 Å and a relatively large diameter within a range of 150 Å to 200 Å is preferred. There is no particular restriction for the raw material of the activated carbon and there can be used, for example, coal, coke, charcoal, coconut shell, wood, resin and bone black. The activated carbon having the pore structure as described above can be prepared by using an activating gas having a steam content from 15% to 60% by volume as an activating condition in the production process of the activated carbon. The efficiency for the adsorptive separation of asphaltene or the like and elimination of mercury can be improved further by using the activated carbon having such a pore structure.

There is no particular restriction for the configuration of the activated carbon and any of shapes such as powder, cylindrical form, globular form, fibrous form or honeycomb may be used. Pelleted carbon or molded carbon can be prepared by adding from 30 parts to 60 parts of petroleum pitch or coaltar as a binder based on 100 parts of carbon material, kneading, molding and then activating them in accordance with an ordinary method.

The activated clay is obtained by treating acidic clay as a sort of clays with sulfuric acid or the like to further improve the activity. An activated clay having a chemical composition comprising SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO and K₂O and having a pore structure with a specific surface area from 500 m²/g to 2500 m²/g, a pore diameter from 5 Å to 500 Å and an average pore diameter from 50 Å to 150 Å can be used as a porous inorganic adsorbent in the first adsorption treatment zone in the present invention.

The silica gel used in the first adsorption treatment zone in the present invention is prepared by coagulating a colloidal solution of silicic acid. The silica gel contains silicon dioxide as the main ingredient, has a pore structure with a specific surface area from 550 m²/g to 700 m²/g, and a pore volume usually of more than 0.3 ml/g, and has a high adsorbability. There is no particular restriction on the configuration and any of powdery, columnar or like other shape may be used like that in the case of the activated carbon.

The zeolite used in the first adsorption treatment zone of the present invention is aluminosilicate which is a material having a three dimensional skeleton and a pore structure formed in the gap thereof. It has a large specific surface area amounting to 500 m²/g or greater and a high adsorbability based thereon. There is no particular restriction for the composition and the structure and any of natural or synthetic products can be used. Further they can be used with no particular restriction on the pore volume, grain size and the configuration, but a pore volume of more than 0.3 ml and the grain size of less than 50 mesh (grain size of more than about 0.3 mm) are preferred. The zeolite mainly comprises an aluminosilicate of alkali metal or alkaline earth metal as described above and constitutes a three dimensional regular skeleton structure having a large cavity, in which an SiO₂ tetrahedron and an AlO₄ tetrahedron of methane structure have one carbon atom in common with each other. The zeolite is specified by the chemical composition and X-ray diffraction pattern. The zeolite has a defined pore diameter within a range from 3 Å to 10 Å depending on the cyclic structure of oxygen and has an adsorbability and molecular sieve property based on the pore structure.

Alumina used in the first adsorption treatment zone of the present invention comprises aluminum oxide as the main ingredient, has a pore structure and shows a high adsorbability at a pore volume usually of more than 0.3 ml/g. Those having a specific surface area of more than 200 m²/g, a pore diameter from 2 Å to 1000 Å and an average pore diameter from 40 Å to 120 Å are used. Alumina having such a pore structure can be prepared by optionally controlling conditions for preparation and aging of aluminum hydrates from alkali aluminates such as sodium aluminate and potassium aluminate, inorganic salts of aluminum such as aluminum sulfate and aluminum nitrate.

Further, the silica-alumina used in the first adsorption treatment zone of the present invention comprises a chemical composition of SiO₂ and Al₂O₃, has a porous structure of composite silica gel and alumina gel, and shows high adsorbability. The silica content in the silica-alumina is selected within the range from 5% to 50% by weight, preferably, 10% to 40% by weight to adjust the acid point. In the present invention, a range from 25% to 30% by weight is particularly preferred. There can be mentioned a specific surface area of more than 200 m²/g, a pore diameter of more than 2 Å and an average pore diameter of more than 100 Å. The silica-alumina having such characteristic values can be prepared by optionally specifying the preparing conditions and the aging conditions of silica-alumina hydrates.

As described above, any of the porous inorganic adsorbents has a porous structure and a large specific surface area and shows a high adsorbability. Particularly, use of a porous material having a specific surface area of more than 100 m²/g, more preferably, from 200 m²/g to 1500 m²/g is preferred since it is possible to improve the adsorptive elimination of asphaltene and mercury eliminating rate.

In the first adsorption treatment zone of the present invention, liquid natural gas condensates and the porous inorganic adsorbent can be brought into contact with each other by any known system such as fixed bed, moving bed, fluidized bed or ebullated bed. According to the fixed bed system, the liquid hydrocarbons can be supplied continuously as an ascending stream or descending stream to a filled layer constituted by filling to fix porous inorganic adsorbent par-

ticles to the adsorption treatment zone to conduct adsorption treatment. On the other hand, according to the moving bed system, the porous inorganic adsorbent particles and the liquid hydrocarbons can be brought into contact with each other continuously while the adsorbent particle group charged from above is successively dropped gravitationally when the adsorbent particles are added intermittently or substantially continuously to one end of the adsorption treatment zone and then taken out intermittently or substantially continuously from the other end. Further, in the fluidized bed or the ebullated bed method, the porous inorganic adsorbent particles are caused to suspend by the stream of the liquid hydrocarbons thereby bringing them into contact with each other. According to the present invention, the fixed bed method is suitable among each of the contact systems described above since the structure of the adsorption treatment zone is simple and the operation is easy as well.

The porous inorganic adsorbent fixed bed can be disposed by filling powdery, pulverized, cylindrical, globular, fibrous or honeycomb-shaped adsorbent in the adsorption treatment zone and fixing in accordance with an ordinary method. Adsorbents having a grain size from 0.5 mm to 4.5 mm can be used. More specifically, a glass wool is laid at the bottom of the adsorption treatment zone and silica balls are disposed to prevent the adsorbent from flowing out of the adsorption treatment zone. The natural gas condensates can be supplied as a descending flow from above or as an ascending flow from below, and brought into contact with the porous inorganic adsorbent in the fixed bed, the descending flow being preferred in view of stabilization of the adsorbent in the adsorption column.

Further, while the porous inorganic adsorbent such as activated carbon, active white clay, zeolite, alumina or silica-alumina can be used alone, two or more of them may be used in admixture.

The conditions for the adsorption treatment in the first adsorption treatment zone can be selected optionally. While an elevated temperature may be used, treatment under a normal temperature is sufficient and the purpose of the adsorption treatment can be attained sufficiently under a normal pressure. Further, in the case of using the fixed bed for the adsorbent, an LV value can be set to less than 100 cm/min, preferably, less than 50 cm/min. The LV value means a value obtained by dividing the amount of the liquid hydrocarbons treated with a cross sectional area of the adsorbent layer.

The mercury content in the liquid hydrocarbons flowing out of the first adsorption treatment zone after the adsorption treatment can be reduced to 4 ppb - 20 ppb although different depending on the kind of the adsorbent used. Further, asphaltene and like other material are adsorbed on the porous inorganic adsorbent and are scarcely present in the liquid hydrocarbons after the adsorption treatment.

The activated carbon used in the second adsorption treatment zone has pore characteristics with a specific surface area of 200 m²/g to 2500 m²/g, a pore diameter from 5 Å to 1000 Å and an average pore diameter from 10 Å to 100 Å. Further, among the activated carbons having such pore characteristics, those having a specific surface area from 500 m²/g to 1500 m²/g, an average diameter from 10 Å to 50 Å and a pore volume from 0.4 ml/g to 1.5 ml/g are particularly preferred for the selective adsorption of mercury.

The raw material for preparing the activated carbon having the pore characteristics described above has no particular restriction and coal, coke, charcoal, bone black or carbonized products such as coconut shell, wood and resin can be used. The activated carbon can be obtained by way of a steam step of activating the carbonized products by using a gas with a steam content of less than 15% by volume.

The gas for activating the activated carbon contains steams and gaseous carbon dioxide. While the content of the gaseous carbon dioxide is not restricted particularly for the activated carbon used in the second adsorption treatment zone of the present invention, it is necessary to activate the carbonaceous material with a gas having a steam content of less than 15% by volume. The activating gas usually used for activating a carbonaceous material has a composition containing steams of 40 % to 60% by volume or higher. This is because the steam partial pressure is set as high as possible for the activating gas composition since the activating rate for the carbonaceous material with steams is much higher than that of the gaseous carbon dioxide. Accordingly, the activating condition for the activated carbon is remarkably moderated in the present invention as compared with that of the conventional method.

The activating gas preferably has a composition comprising 50 % to 85 % by volume of nitrogen gas, 3 % to 15 % by volume of steams, 3 % to 30 % by volume of gaseous carbon dioxide (carbonic acid gas), 0 % to 2 % by volume of oxygen gas and 0 % to 2 % by volume of hydrogen gas. The activating treatment is conducted by heating the carbonaceous material as described above, that is, the carbonaceous material to 700°C - 1200°C in the activating gas followed by cooling. Activated carbon having a specific surface area from 200 m²/g to 2500 m²/g, a pore diameter from 5 Å to 1000 Å, an average pore diameter from 10 Å to 50 Å and a pore volume from 0.4 ml/g to 1.5 ml/g can be obtained by the activating treatment.

Although the details for the mechanism of improving the mercury adsorbability of the activated carbon by the activating condition of low steam content is not always apparent at present, it is supposed that the activated carbon obtained under the activating condition described above has the foregoing pore characteristics, so that pores suitable to the adsorption of mercury have a highly developed pore structure and the performance of eliminating mercury in the liquid hydrocarbons is enhanced by the pore structure. In the activating treatment, it is preferred that the activated carbon is cooled also after the activation in a gas having a similar composition as that of the activating gas till the temperature of the activated carbon is lowered to less than 300°C and then taken out of the system. In this case, the gas similar

with the activating gas, that is, an atmosphere required during cooling may be an atmosphere of a nitrogen gas, gaseous carbon dioxide or a gas mixture thereof used upon activation (content of oxygen or hydrogen of less than 1% - 2%), and it is not always necessary that the gas used for activation and the gas used for cooling have a composition just identical with that of the activating gas.

5 In the second adsorption treatment zone of the present invention, the activated carbon may be used alone or may be used as a mercury adsorbent in which an alkali metal sulfide and/or alkaline earth metal sulfide is carried on the activated carbon subjected to the activating treatment as described above. Such a metal sulfide has an effect of improving the mercury adsorption performance of the activated carbon. There is no particular restriction for the alkali metal sulfide or the alkaline earth metal sulfide carried on the activated carbon and there can be mentioned, for example, Li_2S , Na_2S and K_2S as the alkali metal sulfide and MgS and CaS as the alkaline earth metal sulfide. Such alkali metal sulfide and alkaline earth metal sulfide may be used alone or in admixture of two or more of them, with Na_2S being most preferred among the compounds.

15 The amount of the alkali metal sulfide or the alkaline earth metal sulfide to be carried has no particular restriction and it is preferably within a range from 0.1% to 30% by weight based on the activated carbon. If the carried amount is less than 0.1% by weight, the mercury adsorption performance tends to be lowered and, if the carried amount is more than 30% by weight, the mercury adsorption performance is also lowered. Further, if the carried amount is more than 30% by weight, the mercury adsorption performance of the activated carbon tends to be hindered by the metal sulfide thereby saturating the effect of improving the mercury adsorption performance.

20 In the present invention, contact between the liquid hydrocarbons and the mercury adsorbent in the second adsorption treatment zone may be conducted by any of the fixed bed, moving bed, fluidized bed or ebullated bed system in the same manner as in the first adsorption treatment zone, and the fixed bed system is suitable since the structure of the adsorption treatment zone is simple and the operation is easy as well. The fixed bed can be constituted and disposed in the same manner as the fixed bed in the first adsorption treatment zone.

25 The mercury adsorbent packed layer in the second adsorption treatment zone of the present invention is constituted by filling and fixing the mercury adsorbent comprising the activated carbon as described above. For the packed layer, two or more of mercury adsorbents can be used as the activated mercury adsorbent described above.

30 In the present invention, it is particularly preferred to use an adsorption treatment zone constituted by filling and fixing mercury adsorbent of activated carbon carrying alkali metal sulfide and/or alkaline earth metal sulfide on the activated carbon to the inlet of the adsorption treatment zone, and filling and fixing a mercury adsorbent only consisting of activated carbon to the exit of the adsorption treatment zone. With such a constitution of the packed layer, even when mercury reacted with the metal sulfide is dissolved again on the sulfide carrying activated carbon, it can be captured in the adsorption treatment zone at the succeeding stage, and leaching of sulfur into the liquid hydrocarbons can also be suppressed.

35 The volume ratio between the activated carbon packed layer, and the layer filled with activated carbon carrying, for example, the alkali metal sulfide is preferably 1 part to 2 parts by weight of the latter relative to one part by weight of the former.

40 While the conditions for the adsorption treatment in the second adsorption treatment zone can be selected optionally like that in the first adsorption treatment zone, a sufficient effect for the adsorption treatment can be obtained under the normal temperature and the normal pressure. Further, in the case of the fixed bed, it is preferred to set the LV value to less than 100 cm/min, particularly, less than 50 cm/min.

A natural gas condensate having a mercury content of 20 ppb - 100 ppb, an asphaltene content of 0.5 % to 2 % by weight in supplied to a first adsorption treatment zone described below under the following treating conditions, and then the adsorption-treated natural gas condensate is supplied to a second adsorption treatment zone filled with the adsorbent also described below.

45 First Adsorption Treatment Zone

Adsorbent; activated carbon

50 Prepared from carbonaceous raw material by heating to 700°C - 1200°C in an activating gas with a steam content in excess of 15 % by volume, followed by cooling.

Reaction system; fixed bed system containing an adsorbent having a grain size from 0.5 mm to 2 mm.

55 Second Adsorption Treatment Zone

Adsorbent; activated carbon

Prepared from carbonaceous raw material by heating to 700°C - 1200°C in an activating gas with a steam

content of less than 15 % by volume, followed by cooling.

Reaction system: fixed bed system containing an adsorbent having a grain size from 0.5 mm to 3 mm.

5 Condition for Treatment

LV value: 1 cm/min - 2 cm/min

10 As another embodiment, in the first adsorption treatment zone, an activated clay is, instead of the activated carbon shown above, is preferably used.

The present invention is to be explained more in details with reference to examples and comparative examples.

Asphaltene in the natural gas condensates used in Examples and Comparative Examples were measured quantitatively by dissolving a specimen into organic solvents of toluene and heptane, measuring the absorbance for the resultant solutions by a spectrophotometer at a wavelength of 750 nm in a 50 mm cell with reference to reference solutions 15 of toluene and heptane and using Lambert-Beer's equation: $K = \log T/0.4343$.

Further, the specific surface area was measured by a BET method with a nitrogen gas. The pore volume and pore diameter distribution were calculated based on an isothermal adsorption curve of nitrogen gas measured by BELL-SORB 28SA measuring equipment.

20 Example 1

A natural gas condensate from Australia (density: 0.7418 g/cm³ at 15°C, mercury content: 27.5 ppb, asphaltene content: 1 % by weight) was passed at a normal temperature and at a flow rate of 1 ml/min through a first adsorption treatment column (adsorption glass tube of 10 mm inner diameter, filled with 24 ml of activated carbon A¹ (grain size: 25 2 mm, specific surface area: 1400 m²/g, average pore diameter: 100 Å.

The mercury content in the natural gas condensate obtained from the first adsorption treatment column was reduced to 1 ppb but the content exceeded 1 ppb after a lapse of 3 days and continuous treatment was impossible. The condensate was passed at a normal temperature at a flow rate of 1 ml/min (LV value: 1.2 cm/min) through a second adsorption column (adsorption glass tube of 10 mm inner diameter filled with 24 ml of activated carbon X⁵ shown in 30 Table 1), to obtain a condensate having a mercury content of 0.2 ppb at the exit of the second adsorption column. When the adsorption treatment was conducted continuously, the mercury content in the treated oil could be maintained to less than 1 ppb for 100 days as shown in Table 1.

Example 2

35 The same natural gas condensate as used in Example 1 was passed at a normal temperature and at a flow rate of 1 ml/min through a first adsorption column (adsorption glass tube of 10 mm inner diameter filled with 24 ml of alumina) (grain size: 2 mm, specific surface area: 1400 m²/g, average pore diameter: 90 Å, manufactured by Sumitomo Chemical Co., Ltd.).

40 The mercury content in the condensate obtained from the first adsorption column was 10 ppb. The condensate was passed at a normal temperature and at a flow rate of 1 ml/min through the same second adsorption column as in Example 1, to obtain a condensate having a mercury content of 0.2 ppb at the exit of the second adsorption column. When the adsorption treatment was conducted continuously, the mercury content in the treated oil could be maintained to less than 1 ppb for 100 days as shown in Table 1.

45 Example 3

The same natural gas condensate as used in Example 1 was passed at a normal temperature and at a flow rate of 1 ml/min through a first adsorption column (adsorption glass tube of 10 mm inner diameter filled with 24 ml of silica alumina (grain size: 2 mm, specific surface area: 310 m²/g, average pore diameter: 100 Å)). 50

The mercury content in the condensate obtained from the first adsorption treatment column was 8 ppb. The condensate was passed at a normal temperature and at a flow rate of 1 ml/min through the same second adsorption treatment column as in Example 1, to obtain a condensate having a mercury content of 0.2 ppb at the exit of the second adsorption column. When the adsorption treatment was conducted continuously, the mercury content in the treated oil 55 could be maintained to less than 1 ppb for 100 days as shown in Table 1.

Example 4

The same natural gas condensate as used in Example 1 was passed at a normal temperature and at a flow rate of

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1 ml/min through a first adsorption column (adsorption glass tube of 10 mm inner diameter filled with 24 ml of silica gel (grain size: 2 mm, specific surface area: 1400 m²/g, average pore diameter: 85 Å).

The mercury content in the condensate obtained from the first adsorption column was 8 ppb, which was passed at a normal temperature and at a flow rate of 1 ml/min through the same second adsorption column as in Example 1, to obtain a condensate having a mercury content of 0.2 ppb at the exit of the second adsorption column. When the adsorption treatment was conducted continuously, the mercury content in the treated oil could be maintained to less than 1 ppb for 100 days as shown in Table 1.

Example 5

The same natural gas condensate as used in Example 1 was passed at a normal temperature and at a flow rate of 1 ml/min through a first adsorption column (adsorption glass tube of 10 mm inner diameter filled with 24 ml of zeolite (grain size: 2 mm, specific surface area: 1400 m²/g, average pore diameter: 10 Å, manufactured by Union Showa Co.)

The mercury content in the condensate obtained from the first adsorption treatment column was 7 ppb, which was passed at a normal temperature and at a flow rate of 1 ml/min through the same second adsorption treatment column, to obtain a condensate having a mercury content of 0.2 ppb at the exit of the second adsorption column. When the adsorption treatment was conducted continuously, the mercury content in the treated oil could be maintained to less than 1 ppb for 100 days as shown in Table 1.

Example 6

The same natural gas condensate as used in Example 1 was passed at a normal temperature and at a flow rate of 1 ml/min through a first adsorption column (adsorption glass tube of 10 mm inner diameter filled with 24 ml of activated clay (grain size: 2 mm, specific surface area: 1400 m²/g, average pore diameter: 95 Å (Nikkanite, manufactured by Toyo Hakudo Co.Ltd.)).

The mercury content in the condensate obtained from the first adsorption column was 11 ppb, which was passed at a normal temperature and at a flow rate of 1 ml/min through the same second adsorption column as in Example 1, to obtain a condensate having a mercury content of 0.2 ppb at the exit of the second adsorption column. When the adsorption treatment was conducted continuously, the mercury content in the treated oil could be maintained to less than 1 ppb for 100 days as shown in Table 1.

Example 7

Quite in the same manner as in Example 1 except for using activated carbon B² (grain size: 2 mm, specific surface area: 1400 m²/g, average pore diameter: 100 Å) instead of the activated carbon A in the first adsorption column, a treated oil with a mercury content of 0.2 ppb was obtained from the exit of the second adsorption column. The results are shown in Table 1.

Example 8

Quite in the same manner as in Example 1 except for using activated carbon C³ instead of activated carbon A in the first adsorption column, a treated oil with a mercury content of 0.2 ppb was obtained from the exit of the second adsorption column. The results are shown in Table 1.

Example 9

Quite in the same manner as in Example 1 except for using activated carbon D⁴ instead of activated carbon A in the first adsorption column, the mercury content in the adsorption-treated oil obtained from the first adsorption column was 20 ppb and a treated oil with a mercury content of 0.2 ppb was obtained from the exit of the second adsorption column. The results are shown in Table 1.

Comparative Example 1

Adsorption treatment for the natural gas condensate was conducted quite in the same manner as in Example 1 except for not using the first adsorption column but using only the second adsorption column filled with activated carbon X⁵ (adsorption glass tube of 10 mm inner diameter, filled with 24 ml of activated carbon X⁵). The results of the adsorption treatment are shown in Table 2.

As shown in Table 2, the residual mercury content in the treated oil is high only with the treatment by the activated carbon in the second adsorption column as shown in Table 2.

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Comparative Example 2

The same natural gas condensate as used in Example 1 was passed through a first adsorption treatment column (adsorption glass tube of 10 mm inner diameter filled with 24 ml of activated carbon ⁵) at a normal temperature and at a flow rate of 1 ml/min. The mercury content in the condensates after the obtained from the first adsorption column was 3.7 ppb. The condensate was passed at a normal temperature and at a flow rate of 1 mm/min through a second adsorption column (adsorption glass tube of 10 mm inner diameter filled with 24 ml of activated carbon A¹), but the mercury content in the treated oil was 3 ppb.

10 Comparative Example 3

The procedures were quite identical with those in Comparative Example 2 except for using zeolite instead of the activated carbon A in the second absorption treatment column. The results are shown in Table 2.

15 Comparative Example 4

The procedures were quite identical with those in Comparative Example 2 except for using alumina instead of the activated carbon A in the second absorption treatment column. The results are shown in Table 2.

20 Comparative Example 5

Mercury adsorption treatment was conducted quite under the identical conditions as those in Example 2 except for using activated carbon Y (specific surface area: 1450 m²/g, average pore diameter: 70 Å) (an experimentally manufactured product)) instead of the activated carbon A in the second adsorption treatment column. The results of the adsorption treatment are shown in Table 2. It can be recognized that the size of the average pore diameter of the activated carbon in the second adsorption column is critical for eliminating a trace amount of mercury.

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Table 1

	Examples								
	1	2	3	4	5	6	7	8	9
Liquid hydrocarbon									
Natural gas condensate									
Asphaltene content (wt.%)	1	1	1	1	1	1	1	1	1
Mercury content (ppb)	27.5	27.5	27.5	27.5	27.5	27.5	27.5	27.5	27.5
First adsorption column									
Adsorbent									
	Activated carbon A	Alumina	Silica-alumina	Silicagel	Zeolite	Activated clay	Activated carbon B	Nas/Activated carbon C	Nas/Activated carbon D
Grain size (mm)	2	2	2	2	2	2	2	2	2
Specific surface area (m ² /g)	1410	1380	310	1460	1480	1400	1390	1350	1350
Average pore diameter (Å)	100	90	100	85	10	95	100	100	100
Treated oil									
Mercury content (ppb)	1	10	8	8	7	11	0.7	1	20
Asphaltene content (wt.%)	0	0	0	0	0	0	0	-	-
Treating time *8	3	-	-	-	-	-	3	3	-
Second adsorption column									
Adsorbent									
	Activated carbon X	Activated carbon X	Activated carbon X	Activated carbon X	Activated carbon X	Activated carbon X	Activated carbon X	Activated carbon X	Activated carbon X
Grain size (mm)	2	2	2	2	2	2	2	2	2
Specific surface area (m ² /g)	1400	1400	1400	1400	1400	1400	1400	1400	1400
Average pore diameter (Å)	24	24	24	24	24	24	24	24	24
Treated oil									
Mercury content (ppb)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Treating time *8	100	100	100	100	100	100	100	100	100

*1) - *6) shown in appended sheet.

*8) number of days for treatment till the mercury concentration in the oil after adsorption treatment keeps or exceeds 1ppb.

Table 2

	Comparative Examples				
	1	2	3	4	5
Liquid hydrocarbon					
Natural gas condensate					
Asphaltene content (wt.%)	1	1	1	1	1
Mercury content (ppb)	27.5	27.5	27.5	27.5	27.5
First adsorption column					
Adsorbent	-	Activated ^{*5} carbon X	Activated ^{*5} carbon X	Activated ^{*5} carbon X	Alumina
Grain size (mm)	-	2	2	2	2
Specific surface area (m ² /g)	-	1400	1400	1400	1380
Average pore diameter (Å)	-	12	12	12	90
Treated oil					
Mercury content (ppb)	-	3.7	3.7	3.7	10
Asphaltene content (wt.%)	-	0	0	0	0
Treating time ^{*8}	-	-	-	-	-
Second adsorption column					
Adsorbent	Activated carbon X	Activated carbon A	Zeolite	Alumina	Activated ^{*6} carbon Y
Grain size (mm)	2	2	2	2	2
Specific surface area (m ² /g)	1400	1410	1480	1380	1450
Average pore diameter (Å)	24	100	10	100	70
Treated oil					
Mercury content (ppb)	3.7	3	2	6	1
Treating time ^{*8}	-	-	-	-	2

*1) - *6) shown in appended sheet.

*8) number of days for treatment till the mercury concentration in the oil after adsorption treatment keeps or exceeds 1ppb.

*1: activated carbon A; trial product

*2: activated carbon B; trial product

*3: activated carbon C; carrying 5 % by weight Na_2S as sulfur content on activated carbon A

*4: activated carbon D; carrying 10 % by weight Na_2S as sulfur content on activated carbon A

*5: activated carbon X; manufactured from a carbonization product using coconut shell as the raw material, by heating the carbonization product to 900 °C in the activation gas followed by cooling to less than 300 °C in the same gas composition and then taken out of the system. The activation gas comprised 80 % of nitrogen, 0.2 % of oxygen, 9.8 % of carbon dioxide and 10 % of water vapor.

*6 activated carbon Y: experimentally manufactured product by the inventors.

Examples and Comparative Examples described above show that specific combination of mercury adsorbents is necessary in each of the examples for the elimination of mercury from natural gas condensates in which asphaltene is present together and that long time continuous operation is possible as a result of the specific combination.

According to the present invention, mercury can be eliminated substantially completely over a long period of time from liquid hydrocarbons containing mercury and asphaltene, for example, natural gas condensates even under the coexistence of asphaltene, by bringing the gas condensates into contact in a first adsorption column with at least one of materials selected from the group consisting of activated carbon, activated clay, alumina, silica-alumina, silica gel and zeolite and then bringing them into contact in a second adsorption column with an activated carbon having a specific surface area of not less than 500 m²/g and an average pore diameter from 10 Å to 100 Å.

Claims

1. A process for eliminating mercury and mercury compounds in liquid hydrocarbons comprising:

(a) contacting liquid hydrocarbons containing mercury and mercury compounds, as well as asphaltene in a first adsorption treatment zone, with a porous inorganic adsorbent which is at least one of materials selected from the group consisting of activated carbon, activated clay, alumina, silica gel, silica-alumina and zeolite, and then, (b) contacting the adsorption treated liquid hydrocarbons from said adsorption treatment zone, in a second adsorption treatment zone, with an activated carbon having a specific surface area from 200 m²/g to 2500 m²/g, an average pore diameter from 10 Å to 100 Å, and a pore volume from 0.4 ml/g to 1.5 ml/g.

2. The process for eliminating mercury and mercury compounds in liquid hydrocarbons as defined in claim 1, wherein the liquid hydrocarbons are natural gas condensates.

3. The process for eliminating mercury and mercury compounds in liquid hydrocarbons as defined in claim 1 or 2, wherein the porous inorganic adsorbent has a specific surface area of more than 200 m²/g and a pore diameter from 2 Å to 1000 Å.

4. The process for eliminating mercury and mercury compounds in liquid hydrocarbons as defined in one or more of claims 1 to 3, wherein the activated carbon used in the first adsorption treatment zone has an average pore diameter more than 100 Å.

5. The process for eliminating mercury and mercury compounds in liquid hydrocarbons as defined in one or more of claims 1 to 4, wherein the activated carbon used in the second adsorption treatment zone has a pore volume from 0.6 ml/g to 1.2 ml/g.

6. The process for eliminating mercury and mercury compounds in liquid hydrocarbons, defined in one or more of claims 1 to 5, wherein the activated carbon used in the second adsorption treatment zone has an average pore diameter of 10 Å to 50 Å.

7. The process for eliminating mercury and mercury compounds in liquid hydrocarbons as defined in one or more of claims 1 to 6, wherein an activated carbon used in the second adsorption treatment zone is obtained by subjecting a carbonaceous material to an activating treatment using an activating gas with a steam content of less than 15 % by volume.

8. The process for eliminating mercury and mercury compounds in liquid hydrocarbons as defined in one or more of claims 1 to 5 and 7, wherein the activating treatment for the carbonaceous material comprises heating the carbonaceous material in an activating gas comprising 50 % to 85 % by volume of nitrogen gas, 3 % to 15 % by volume of steam, 3 % to 30 % by volume of gaseous carbon dioxide, 0 % to 2 % by volume of oxygen gas, 0 % to 2 % by volume of hydrogen gas, to a temperature of 700 °C to 1200 °C followed by cooling, thereby preparing an activated carbon having a specific surface area from 200 m²/g to 2500 m²/g and an average pore diameter from 10 Å to 100 Å.

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- 5 9. A process for eliminating mercury and mercury compounds in liquid hydrocarbons as defined in one or more of claims 1 to 8, wherein the mercury-containing liquid hydrocarbons are brought into contact with the solid adsorbent in the first adsorption treatment zone and the activated carbon in the second adsorption treatment zone each having a grain size from 0.15 mm to 4.75 mm.
- 10 10. The process for eliminating mercury and mercury compounds in liquid hydrocarbons as defined in one or more of the preceding claims wherein the activated clay is used in the first adsorption zone and the activated carbon is used in the second adsorption zone.

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